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METHOD FOR MANUFACTURING STARCH FIBER COMPOUNDED WITH FINE PARTICLES

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[There are no amendments to this patent.]

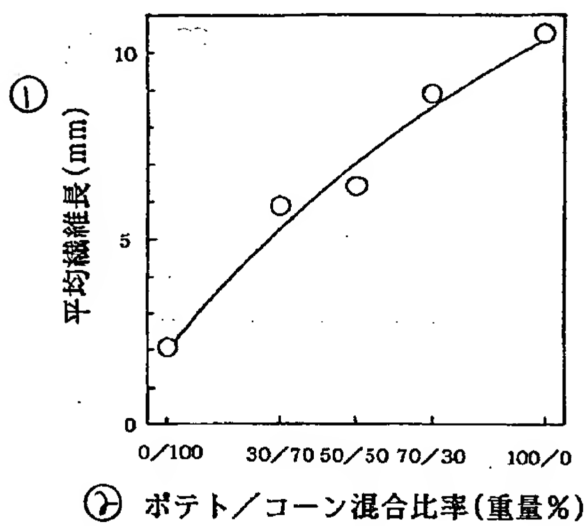
Abstract

Purpose

The purpose of this invention is to provide a method for manufacturing starch fiber compounded with fine particles characterized by the fact that the fiber length can be controlled at will irrespective of the compounded fine particles.

Constitution

A method for manufacturing starch fiber compounded with fine particles characterized by the following facts: starch fiber compounded with fine particles is manufactured by spinning a mixed colloidal dispersion consisting of starch and fine particles; the proportion of raw material fine particles is 90 wt% or less with respect to the total weight of the starch and fine particles; a mixture of a spinnable starch and a nonspinnable starch is used as the raw material starch; by changing the mixing ratio of the spinnable starch and the nonspinnable starch, one can control the average fiber length of the obtained starch fiber compounded with fine particles at will.



Key: 1 Average fiber length (mm)
2 Mixing ratio of potato/corn (wt%)

Claims

1. A method for manufacturing starch fiber compounded with fine particles characterized by the following facts: starch fiber compounded with fine particles is manufactured by spinning a mixed colloidal dispersion consisting of starch and fine particles; the proportion of raw material fine particles is 90 wt% or less with respect to the total weight of the starch and fine particles; a

mixture of a spinnable starch and a nonspinnable starch is used as the raw material starch; by changing the mixing ratio of the spinnable starch and the nonspinnable starch, one can control the average fiber length of the obtained starch fiber compounded with fine particles at will.

2. The method for manufacturing starch fiber compounded with fine particles described in Claim 1 characterized by the fact that it makes use of potato starch as the spinnable starch, and cornstarch as the nonspinnable starch.

3. The method for manufacturing starch fiber compounded with fine particles described in Claim 1 characterized by the fact that the mixing proportion of raw material fine particles with respect to the sum weight of starch and fine particles is in the range of 30-70 wt%.

Detailed explanation of the invention

[0001]

Technical field of the invention

This invention pertains to a method for manufacturing starch fiber compounded with fine particles. More specifically, this invention pertains to a method for manufacturing starch fiber compounded with fine particles characterized by the fact that by selecting the amount of fine particles for compounding, one can obtain a starch fiber compounded with fine particles having any desired average fiber length corresponding to the specific application.

[0002]

Prior art

Starch fibers prepared from starch in pulp form have been used as a material for entirely or partially substituting wood fibers. When starch fibers are mixed with wood pulp in making paper, the strength characteristics of the obtained paper can be improved, and retentivity of the chemicals added in manufacturing the paper can be increased. Also, the transparency of starch fibers is exploited in manufacturing glassine paper from a mixture with wood pulp.

[0003]

Several methods may be adopted in manufacturing said starch fibers. In one method, an aqueous suspension of starch is heated or treated with an alkali to form a colloidal dispersion of starch. Then, the colloidal dispersion of starch is extruded and solidified to form yarns in a solidification bath consisting of an aqueous solution of ammonium sulfate or the like. In another method, an aqueous suspension of starch is converted to a starch colloidal dispersion by means of boiling dissolution using the jet cooking method, and is then solidified in a solidification bath (for example, see: US Patent No. 4139699, Japanese Kokoku Patent No. Sho 60[1985]-35480, Japanese Tokuhyo Patent Application No. Hei 7[1995]-502312, etc.).

[0004]

As far as the fiber length of the starch fibers manufactured in the aforementioned methods is concerned, the starch fibers described in Japanese Tokuhyo Patent Application No. Hei 7[1995]-502312 are 1 mm or shorter, and the starch fibers described in Japanese Kokoku Patent No. Sho 60[1985]-35480 have a length in the range of 0.1-3.0 mm. However, when used in the paper making field, starch fibers leak through the wire in the paper making operation if they are too short, and the desired purpose cannot be realized. On the other hand, if the fibers are too long, they bundle together and result in lumps in the formed paper. This is undesired.

[0005]

In order to solve the aforementioned problems, the present inventors performed extensive research. As a result of this research, a method for manufacturing starch fibers with any desired length was developed and filed for patent application (Japanese Patent Application No. Hei 6[1994]-154672). The invention of this preceding patent application concerns two types of raw material starch, spinnable and nonspinnable, which provide long starch fibers and short starch fibers, respectively. When the two types are mixed appropriately to form a raw material starch, starch fibers with any desired fiber length distribution can be obtained corresponding to the mixing ratio. By using starch fibers with the desired fiber length distribution, the desired application purpose can be realized effectively, and effects that cannot be realized in the prior art can be obtained.

[0006]

Also, said Japanese Kokoku Patent No. Sho 60[1985]-35480 described a method in which a water-insoluble additive, e.g., pigment, metal powder, latex, etc., is added homogeneously to the entirety of a starch dispersion, so that it is enclosed in starch fibers. In addition, Japanese Tokuhyo Patent Application No. Hei 7[1995]-50231 described a method in which an organic thickener and mineral are added to a starch suspension.

[0007]

Problems to be solved by the invention

However, in the aforementioned method in which a water-insoluble additive is included in the starch fibers, the fiber length of the starch fibers is a problem. For example, when a pigment or other powder additive is used to impart certain functions to the starch fibers, the fiber length of the starch fibers has to be controlled to realize the desired application purpose. Also, in some cases, a large amount of the additive must be added to the starch fibers in order to manifest

the functions. However, even when a large amount can be added, if the fiber length of the starch fibers cannot be controlled at will, starch fibers with a high additional value still cannot be obtained.

[0008]

The purpose of this invention is to provide a method for manufacturing starch fibers compounded with fine particles characterized by the fact that any desired fiber length can be realized at will, and the amount of fine particles can be selected in a wide range.

[0009]

Means to solve the problems

As a result of extensive studies by the present inventors, it was found that in a system with added fine particles, by mixing spinnable starch and nonspinnable starch at an appropriate mixing ratio, one can control the fiber length distribution at will corresponding to this mixing ratio, and said characteristics can be maintained even when the proportion of fine particles is very large. In this way, the present invention was reached.

[0010]

This invention provides a method for manufacturing starch fiber compounded with fine particles characterized by the following facts: starch fiber compounded with fine particles is manufactured by spinning a mixed colloidal dispersion consisting of starch and fine particles; the proportion of raw material fine particles is 90 wt% or less with respect to the total weight of the starch and fine particles; a mixture of a spinnable starch and a nonspinnable starch is used as the raw material starch; by changing the mixing ratio of the spinnable starch and the nonspinnable starch, one can control the average fiber length of the obtained starch fiber compounded with fine particles at will.

[0011]

Embodiment of the invention

According to this invention, "fine particles" refers to objects with small dimensions for observation under a microscope. Typically, "fine" refers to the fineness that can be distinguished under a microscope. "Particles" refers to objects with small dimensions, that is, length, width, and thickness, that can be observed according to JIS Z8122. For example, solid particles may be roughly divided into two types according to the manufacturing methods, that is, for both natural substances and synthetic substances, the type prepared by crushing large lumps and the type prepared by means of a chemical reaction. The types may be further divided as follows: fine

particles prepared by crushing a solid; fine particles prepared by oxidation, reduction, pyrolysis, or other chemical reaction; fine particles prepared by precipitation or electrodeposition from a liquid; fine particles prepared by spray solidification from the melt state; fine particles prepared by condensation from a vapor; and fine particles prepared by pyrolysis of the vapor of a chemical; etc. Any of these types of fine particles may be used preferably as the fine particles in this invention.

[0012]

Examples of fine particles that can be used in this invention include metal powders of aluminum, silicon, titanium, chromium, iron, cobalt, nickel, copper, zinc, silver, tin, tungsten, platinum, gold, etc.; kaolinite, halocite, sericite, zeolite, diatomaceous earth, and other clay mineral powders; magnesium oxide, acetylene black, barium ferrite, graphite, magnetic toner, and other electrical/magnetic powders; white carbon, titanium oxide, zinc oxide, calcium carbonate, fine particles of anhydrous silica, copper phthalocyanine blue, zinc sulfite calcium phosphor, and other organic and inorganic filler powders; acrylate nylon, MBS resin, plastic pigment, polyethylene, microcapsules, and other organic polymer powders; microfibrillated cellulose, crystalline cellulose, and other fine fibers; fine powders prepared from the residue after extraction of coffee, green tea, black tea, etc.; latex, emulsion, etc. As needed, two or more types of said fine particles may be mixed for use.

[0013]

It is preferred that the amount and particle size of the fine particles and their combination be determined in preparatory experiments to realize preferable conditions corresponding to the specific application. For the fine particles, the size depends on the size of the starch fibers compounded with fine particles to be manufactured. The size should be smaller than the diameter of the nozzle used in the spinning operation. Typically, the size should be 100 μm or smaller, or preferably 50 μm or smaller. In particular, for particles with a size of 1 μm or smaller, secondary coagulation takes place easily due to the surface activity energy. Consequently, as needed, one should add a cationic surfactant, anionic surfactant, nonionic surfactant, or amphoteric surfactant in an appropriate amount to prevent secondary coagulation.

[0014]

According to this invention, for the nonspinnable starch, starch fibers with an average fiber length distribution of about 1 mm or shorter are obtained when prepared using the following method. On the other hand, for the spinnable starch, starch fibers with an average fiber length distribution of about 15 mm or longer are obtained.

[0015]

The method for preparing starch fibers determining nonspinnability is as follows. First of all, an aqueous suspension with 10 wt% starch is prepared. The aqueous suspension is heated to 95°C to form a colloidal dispersion of swelled starch. The dispersion is kept at a constant temperature of 55°C, and it is ejected from a nozzle with a diameter of 0.4 mm and set in a solidification bath under a pressure of 3 kg/cm^2. The solidification solution used in the solidification bath is a 40 wt% aqueous solution of ammonium sulfate. While the solidification bath is agitated, the starch dispersion is ejected at an angle of 45° between the ejecting direction of the starch dispersion and the flow direction of the solidification solution.

[0016]

The average fiber length distribution of the starch fibers is measured using the following method. The starch fibers prepared above are taken out from the solidification bath and spread on a specimen for drying and solidification. Then, the length of each fiber is measured using a map meter for the image enlarged with a projector. About 200 starch fibers are solidified for each specimen. In each test, 10 specimens are prepared. For each type of starch, tests are performed three times, and the average fiber length distribution is determined from the measurement results.

[0017]

When the aforementioned method is adopted to prepare starch fibers from starch in practice, it has been found that one can distinguish between the spinnable starch and the nonspinnable starch. The following are examples of the types of starch determined by the present inventors.

[0018]

Spinnable starches: potatoes, cassava, taro, sweet potatoes, Chinese yams, white yams, yautia, water chestnuts, tamus, guinea yams, Indian Alocasia, kiltosburma [transliteration], etc.

[0019]

Nonspinnable starches: corn, wheat, rice, barley, rye, oats, sorghum, Indian millet, Japanese millet, millet, etc.

[0020]

Generally speaking, starches derived from stems and roots of plants are spinnable, while starches derived from grains are not. However, when starch fibers are actually prepared, caution

should be exercised with regard to the starches to be used. All the above-listed starches are natural starches. However, the invention is not limited to the use of natural starches. Processed starches and other modified starches may also be used after determining their nonspinnability.

[0021]

When the invention is embodied, first of all, one or several types of fine particles and spinnable starch as well as nonspinnable starch are mixed at any desired ratio to prepare a mixed aqueous suspension of fine particles and starch particles. The suspension is then heated to swell the starch to form a mixed colloidal dispersion of fine particles and starch. When the concentration of starch in the fine particles/starch mixed aqueous suspension is low, the coagulating strength is low in spinning. On the other hand, when the concentration of starch is high, after swelling of the starch, the fine particles/starch mixed colloidal dispersion loses its fluidity, and spinning cannot be performed. As a result of the experiment, it should be determined whether there is any change in the fluidity of the colloidal dispersion due to mixing of the fine particles. Typically, it is possible to have a better fluidity when fine particles are not added, and it is possible to increase the concentration of the starch. However, depending on the type of fine particles, the fluidity may be hindered when the average particle size is 1 μm or smaller. In some cases, one may have to add a dispersing agent to realize a good fluidity. The concentration of the solid component (starch + fine particles) in the fine particles/starch mixed aqueous suspension changes depending on the type of starch. However, in consideration of the experimental results, the concentration of the solid component is preferably in the range of 5-20 wt%. When the mixing proportion of the fine particles is increased, the concentration of the solid component in the fine particles/starch mixed aqueous suspension increases. When the mixing proportion of the fine particles is decreased, the concentration of the solid component in the fine particles/starch mixed aqueous suspension decreases. The time and temperature for heating the mixed aqueous suspension should be appropriate to ensure sufficient swelling of the starch to realize gelatinization. Typically, a temperature of 100°C or lower may be adopted.

[0022]

As far as the mixing proportion of the fine particles is concerned, the proportion of fine particles with respect to the sum weight of starch and fine particles should be 90 wt%. If the proportion of fine particles is over 90 wt%, the obtained starch fibers compounded with fine particles are not well formed. On the other hand, the lower limit of the proportion of fine particles changes depending on the type of the fine particles. That is, for some types of fine particles, an amount of about 1 wt% cannot display the mixing effect. For some other types of fine particles, even for an amount as small as about 0.1 wt%, the mixing effect can already be

manifested. In any case, one should add the fine particles in an amount greater than the smallest amount for displaying the mixing effect. Typically, the mixing proportion of the fine particles with respect to the sum weight of starch and fine particles should be in the range of 30-70 wt%.

[0023]

After cooling of the fine particles/starch mixed colloidal dispersion prepared with swelled starch, spinning is performed while the prescribed temperature is maintained. It is preferred that the temperature of the mixed colloidal dispersion be maintained at 50-60°C during spinning. If the temperature of the mixed colloidal dispersion varies, the viscosity changes, and it is impossible to obtain the starch fibers compounded with fine particles with a high stability. Also, it has been found that when the temperature decreases significantly, the starch ages.

[0024]

Then, the fine particles/starch mixed colloidal dispersion kept at a prescribed temperature is loaded in a sealed container, and a prescribed pressure is applied so that the fine particles/starch mixed colloidal dispersion is ejected from a nozzle having any desired number of holes and hole diameter and shape into a solidification bath. In this so-called wet spinning method, starch fiber compounded with fine particles can be formed. The wet spinning method is a conventional method commonly adopted in spinning viscose fibers, etc. A conventional spinning device may be adopted. The diameter (size) of the starch fibers compounded with fine particles can be adjusted by changing the hole diameter of the nozzle.

[0025]

Examples of the solidification solutions for the solidification bath include aqueous solutions of ammonium sulfate, sodium sulfate, magnesium sulfate, ammonium phosphate, sodium carbonate, ammonium chloride, and other salts that can generate electrolytes in water. From these, ammonium sulfate is preferred. If the concentration of the solidification solution is too low, a sufficient coagulation effect cannot be realized. Typically, the concentration of the salt aqueous solution should be in the range of 30-40 wt%.

[0026]

The solidification solution in the solidification bath is agitated continuously to generate a flow of the solidification solution. The flow direction and velocity of the solidification solution affect the length and strength of the starch fibers compounded with fine particles. That is, it is preferred that the ejecting direction of the mixed colloidal dispersion and the direction of the solidification solution be in agreement with each other so that the fine particles/starch mixed

colloidal dispersion ejected into the solidification solution forms a stable flow of yarns. However, when they are not in agreement with each other due to the design of the device, one should have an angle of 90° or smaller between the ejecting direction and the flow direction of the solidification solution. Also, by drawing the yarns with a flow velocity of the solidification solution is higher than the ejecting velocity of the mixed colloidal dispersion, one can make the starch fibers compounded with fine particles insoluble in water and increase their strength. However, if the flow velocity of the solidification solution is too high, yarns tear apart in the solidification bath, and it is impossible to obtain starch fibers compounded with fine particles having the desired fiber length. For this reason, it is necessary to determine the flow direction and flow rate of the solidification solution appropriately in preparatory experiments for obtaining the desired starch fibers compounded with fine particles.

[0027]

As an example of application of the starch fibers compounded with fine particles obtained in this invention, starch fibers compounded with a white pigment, such as titanium dioxide, can be used in forming paper to improve the opaqueness of the paper as the transparency of the starch fibers can be shielded with the white pigment. In addition, starch fibers compounded with fine electroconductive particles may be used in manufacturing static inhibiting paper.

[0028]

Application examples

In the following, this invention will be explained in detail with reference to application examples.

[0029]

Application Example 1

A mixed aqueous suspension with a solid component content of 10 wt% was prepared from 5 wt% kaolin clay (commercial name "SF Kaolin", product of Hattori Mining Co., Ltd.) and 5 wt% of a mixture of potato starch and cornstarch at one of several mixing ratios. The aqueous mixture suspension was heated at 95°C so that the starch swelled to form a fine particles/starch mixed colloidal dispersion. A circular 0.3-mm nozzle was set in a solidification bath containing a solidification solution consisting of 40 wt% of an aqueous solution of ammonium sulfate. Then, said fine particles/starch mixed colloidal dispersion was ejected at a constant temperature of 55°C and under an ejecting pressure of 2 kg/cm^2 from the nozzle into the solidification solution to manufacture a starch fiber compounded with fine particles. During

ejection, the solidification bath was agitated, and the angle between the ejecting direction of the fine particles/starch mixed colloidal dispersion and the flow direction of the solidification solution was 30°.

[0030]

Table 1 and Figure 1 illustrate the relationship between the starch fibers compounded with fine particles prepared from potato starch (potato) and cornstarch (corn) at various mixing ratios and the average fiber length direction of the starch fibers compounded with fine particles.

[0031]

Table 1

① デンプン混合比率（重量%）［ポテト／コーン］	② 平均繊維長分布（mm）
0／100	2．1±0．23
30／70	5．9±0．54
50／50	6．4±0．49
70／30	8．9±0．75
100／0	10．5±1．8

Key: 1 Starch mixing ratio (wt%) (Potato/corn)
2 Average fiber length distribution (mm)

As can be seen from Table 1 and Figure 1, as the proportion of spinnable potato starch is increased, the average fiber length increases. On the other hand, when the proportion of the nonspinnable corn starch is increased, the obtained starch fibers compounded with fine particles have a small average fiber length.

[0032]

Application Example 2

Mixed aqueous suspensions with a solid component content of 10 wt% were prepared from a mixture of potato starch and cornstarch at a fixed mixing ratio of 50:50 by weight, kaolin and clay (as aforementioned) at various mixing ratios of the starch mixture. Otherwise, the operation was performed in the same way as in Application Example 1 to form starch fibers compounded with fine particles.

[0033]

Table 2 illustrates the relationship between the mixing ratio of starch (50:50 mixture of potato starch and cornstarch by weight) and the average fiber length direction of the obtained starch fibers compounded with fine particles.

[0034]

Table 2

① デンプンと微細粒子の混合比率（重量%）［デンプン／微細粒子］	② 平均繊維長分布（mm）
10／90	0．5±0．04
30／70	4．2±0．56
50／50	6．4±0．49
70／30	7．6±0．33
90／10	10．7±1．54
100／0	11．6±1．83

Key: 1 Mixing ratio of starch to fine particles (wt%) (starch/fine particles)
2 Average fiber length distribution

As can be seen from Table 2, even when the proportion of fine particles is 90 wt%, mixing still can be performed. In this case, the starch fibers compounded with fine particles display a fiber shape as observed under a microscope.

[0035]

<u>Application Example 3</u>

Mixed aqueous suspensions with a solid component content of 10 wt% were prepared from titanium oxide (commercial name "Tibake W-10", product of Ishihara Industry Co., Ltd.) and starch mixtures of potato starch and cornstarch in various mixing ratios. Otherwise, the operation was performed in the same way as in Application Example 1 to form starch fibers compounded with fine particles.

[0036]

Table 3 illustrates the relationship between the mixing ratios of titanium oxide, potato starch (potato) and cornstarch (corn) and the average fiber length direction of the obtained starch fibers compounded with fine particles.

[0037]

Table 3

① 酸化チタン (重量%)	② デンプン混合比率 (重量%) [ポテト/コーン]	③ 平均繊維長分布 (mm)
30	70 [30/70]	5. 5±0. 61
50	50 [50/50]	5. 4±0. 45
70	30 [70/30]	5. 2±0. 88

Key: 1 Titanium oxide (wt%)
2 Mixing ratio of starches (wt%) (potato/corn)
3 Average fiber length distribution

As can be seen from Table 3, even when the proportion of fine particles is changed, by changing the mixing ratio of the spinnable starch to the nonspinnable starch, one can realize almost the same average fiber length distribution.

[0038]

Effects of the invention

The invention explained above has the following effects.

1) By changing the mixing ratio of the spinnable starch to the nonspinnable starch, one can control the average fiber length distribution of the obtained starch fibers compounded with fine particles to any range.

2) The mixing proportion of the fine particles can be as high as about 90 wt%.

3) As the fiber length can be adjusted corresponding to the specific application of the starch fibers compounded with fine particles, one can realize effects that cannot be obtained with conventional starch fibers. As a result, one can expand the application of starch fibers.

Brief description of the figures

Figure 1 is a graph illustrating the relationship between the mixing ratio of the potato starch (potato) to the cornstarch (corn) and the average fiber length of the obtained starch fibers compounded with fine particles when the mixing proportion of the fine particles with respect to the sum weight of the starch and the fine particles (kaolin clay) is kept constant at 50 wt%.

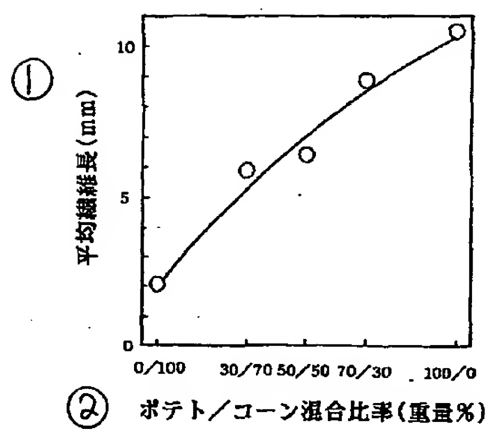


Figure 1

Key: 1 Average fiber length (mm)
2 Potato/corn mixing ratio (wt%)